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<p>(21) International Application Number: PCT/EP00/04216 (22) International Filing Date: 4 May 2000 (04.05.00) (30) Priority Data: 99303622.7 10 May 1999 (10.05.99) EP (71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): BROEKHUIS, Antonius, Augustinus [NL/NL]; (NL). DIRKZWAGER, Hendrik [NL/NL]; (NL). HEERES, Hero, Jan [NL/NL]; (NL). VAN DER LINDEN, Adrianus, Johannes [NL/NL]; (NL). MUL, Wilhelmus, Petrus [NL/NL]; (NL). PELLO, Dennis, Humphrey, Louis [NL/NL]; (NL). SERVAAS, Sjoerd, Carel [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).</p>	<p>(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	
<p>(54) Title: PROCESS FOR THE PREPARATION OF COPOLYMERS OF CARBON MONOXIDE AND OLEFINICALLY UNSATU- RATED COMPOUNDS (57) Abstract A copolymerization process for copolymerising carbon monoxide and an olefin employs a catalyst comprising a Group VIII metal, for example palladium, and a bidentate ligand having general formula <math>R^1R^2M^1-R-M^2R^3R^4</math> where R represents a bridging group, <math>M^1</math> and <math>R^2</math> represent nitrogen, arsenic, antimony or, preferably phosphorus, and <math>R^1</math>, <math>R^2</math>, <math>R^3</math> and <math>R^4</math> preferably represent phenyl groups each having an alkoxy substituent and a sulphonyl substituent <math>-SO_2-OH</math> or a salt or ester derivative. Such catalysts afford good reaction rates and good recycling properties.</p>		

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PROCESS FOR THE PREPARATION OF COPOLYMERS OF CARBON  
MONOXIDE AND OLEFINICALLY UNSATURATED COMPOUNDS

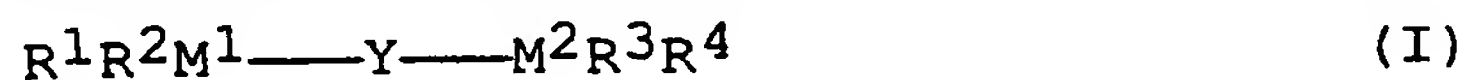
The present invention relates to a process for the preparation of copolymers of carbon monoxide and one or more olefinically unsaturated compounds, to copolymers prepared by such a process, and to the use of such  
5 copolymers.

Copolymers of interest in relation to the present invention are described, for example, in EP-A-121965, EP-A-248483, EP-A-743336 and WO96/13549, and also described therein are catalyst compositions useful for  
10 the preparation of the copolymers, and uses to which the copolymers may be put. The catalyst compositions are based on a Group VIII metal and a dentate ligand which can be indicated by the general formula



In this formula  $M^1$  and  $M^2$  independently represent a  
15 phosphorus, nitrogen, arsenic or antimony atom, each group R may be selected from a wide variety of organic groups, for example optionally substituted alkyl, aralkyl, cycloalkyl or, preferably, aryl groups and Y represents a bivalent bridging group.

The present invention provides a copolymerization  
20 process comprising the step of copolymerizing carbon monoxide and an olefinically unsaturated compound in the presence of a catalyst composition based on a Group VIII metal and a dentate ligand having the general formula



25 where  $M^1$  and  $M^2$  independently represent one of phosphorous, nitrogen, arsenic and antimony,  $R^1$  represents an aryl group having a substituent of the

general formula  $-S(O)_n-X$ , in which  $n$  represents 0, 1 or 2 and  $X$  represents a hydroxy group, which aryl group is optionally further substituted;  $R^2$ ,  $R^3$  and  $R^4$  independently represent an optionally substituted alkyl group or optionally substituted aryl group, on the understanding that at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  represents an aryl group having a substituent or a further substituent selected from hydroxy, alkoxy and alkoxyalkoxy; and  $Y$  represents a bridging group; or an ester or salt derivative of such a ligand.

Generally, unless stated otherwise in this specification, any aryl substituent or aryl moiety of a group may comprise up to 20 ring carbon atoms, preferably up to 10 ring carbon atoms (excluding substituents). A preferred optionally substituted aryl group is an optionally substituted phenyl group.

Generally, unless otherwise stated in this specification, any substituted aryl group of a compound of formula I may suitably be substituted by 1-3 substituent(s). Generally, unless otherwise stated, any said further substituent of an aryl group may be any one of the group comprising halogen, especially fluorine, chlorine and bromine atoms, and nitro, cyano, hydroxy, alkyl, haloalkyl, haloalkoxy, alkoxyalkyl, aryloxy, alkoxy, alkoxyalkoxy, amino, mono- and di-alkylamino, aminoalkyl, mono- and di-alkylaminoalkyl, amido, mono- and di-alkylamido groups, alkylthio, alkylsulphonyl, dialkylamidodsulphonyl and alkylsulphonate groups. It is preferred for any of the aryl groups mentioned above, that it has at least one such further substituent selected from hydroxy, alkoxyalkoxy and, especially, alkoxy.

Generally unless otherwise stated in this specification, any alkyl group or alkyl moiety of a group

may be linear, branched or cyclic and may suitably contain 1 to 24, preferably 1 to 12, most preferably 1 to 6, and especially 1 to 4, carbon atoms, suitable examples being methyl, ethyl and propyl.

5 Preferably,  $n$  is 2. Thus, preferred ligands are sulphonic acids, or esters or salts thereof, more preferably acids or salts, most preferably salts thereof.

Preferred salts of the ligands of general formula I are metal salts, for example alkali metal salts.

10 The sulphonated compounds as used in the method of the invention may include zwitterionic forms; for example with some ligands having phosphorus or nitrogen atoms  $M^1$  and  $M^2$  and a plurality of sulphonyl groups both phosphorus or nitrogen atoms may be protonated whilst two  
15 sulphonic acid groups may be deprotonated.

Suitably  $R^1$  has a said further substituent, preferably at the 2- position.

Preferably  $R^1$  is further substituted by one or more groups independently selected from hydroxy, alkoxyalkoxy  
20 and, especially, alkoxy, and preferably by only one such further group.

Preferably any one of  $R^2$ ,  $R^3$  and  $R^4$  represents independently an aryl group having a substituent of the general formula  $-S(O)_n-X$ , which aryl group is optionally  
25 further substituted, preferably by one or more groups independently selected from hydroxy, alkoxyalkoxy and, especially, alkoxy, and more preferably by only one such further group.

Preferably an aryl group  $R^2$ ,  $R^3$  or  $R^4$  has a said  
30 further substituent, preferably at the 2- position.

Preferably, any substituent of general formula  $-S(O)_n-X$  is located at a meta position relative to the linkage to the respective group  $M^1$  or  $M^2$ . Preferably, a

substituent of general formula  $-S(O)_n-X$  is located at the para position relative to a further substituent of the aryl group. Thus, a preferred group  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  has a substituent, preferably an alkoxy group, especially methoxy, at the 2-position and a substituent of general formula  $-S(O)_n-X$  at the 5-position.

Preferably, a group  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  having a substituent  $-S(O)_n-X$  has only one substituent of this formula.

Preferably, at least one of  $R^1$  and  $R^2$  and at least one of  $R^3$  and  $R^4$  represents an aryl group having a substituent of general formula  $-S(O)_n-X$  and at least one said further substituent. Preferably each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  represents such a group.

The bridging group Y preferably contains, in addition to hydrogen atoms, 1 to 12 atoms of which: up to 4 may be hetero atoms; and at least 1 is a bridging atom. By "bridging atom(s)" is meant atom(s) directly linking between groups  $M^1$  and  $M^2$ . Preferably there are from 2 to 4 bridging atoms. Bridging atoms may be selected from C, N, O, Si and S atoms. Preferably R is an organic bridging group containing at least one bridging atom which is typically carbon. More preferably R is an organic bridging group containing from 2 to 4 bridging atoms, at least two of which are carbon atoms. Examples of such groups R are  $-CH_2-CH_2-$ ,  $-CH_2-CH_2-CH_2-$ ,  $-CH_2-C(CH_3)_2-CH_2-$ ,  $-CH_2-C(C_2H_5)_2-CH_2-$ ,  $-CH_2-Si(CH_3)_2-CH_2-$  and  $-CH_2-CH_2-CH_2-CH_2-$ .

At least one of  $M^1$  or  $M^2$  preferably represents a phosphorus atom. More preferably, both of  $M^1$  and  $M^2$  represents a phosphorus atom.



Ligands in accordance with the present invention for use in a catalyst composition preferably form a complex with the Group VIII metal. It would appear that the presence of two complexing sites in one ligand molecule significantly contributes to the activity of the catalysts.

Preferred ligands include 1,3-bis[bis(2-methoxy-5-sulphophenyl)phosphino]propane, 1,3-bis[bis(2-methoxy-5-sulphophenyl)phosphino]-2,2-dimethylpropane and 1,3-bis[bis(2-methoxy-5-sulphophenyl)phosphino]-2,2-diethylpropane, and salts thereof. Salts of such ligands, in particular alkali metal salts and notably sodium salts, appear to be more effective for polymerization processes than the free acids. The term "sulpho" is used herein to denote sulphonic acid groups  $\text{-SO}_2\text{-OH}$  whilst the term "sulphonato" denotes salts. The skilled person will take note of the fact that ligands denoted by nomenclature may, in fact, exist in zwitterionic forms.

The amount of a said dentate ligand supplied may vary considerably, but is usually dependent on the amount of Group VIII metal present in the catalyst composition. Preferred amounts of a said phosphorus-containing dentate ligand are in the range of from 0.5 to 1.5 moles per gram atom of Group VIII metal.

Generally, unless otherwise stated, the Group VIII metal (in more modern nomenclature a Group 8, 9 or 10 metal) may comprise nickel or cobalt. However, the Group VIII metal is preferably a noble Group VIII metal, of which palladium is most preferred.

A Group VIII metal is typically employed as a cationic species. As the source of Group VIII metal cations conveniently a Group VIII metal salt is used. Suitable salts include salts of mineral acids, such as sulphuric acid, nitric acid, phosphoric acid, perchloric acid and sulphonic acids, and organic salts, such as

acetylacetonates. Preferably, a salt of a carboxylic acid is used, for example a carboxylic acid with up to 8 carbon atoms, such as acetic acid, trifluoroacetic acid, trichloroacetic acid, propionic acid and citric acid. Palladium (II) acetate and palladium (II) tri-fluoroacetate represent particularly preferred sources of palladium cations. Another suitable source of Group VIII metal cations is a compound of the Group VIII metal in its zero-valent state.

Such a Group VIII metal containing catalyst composition may, as an optional measure, be based on another additional component which functions during the copolymerization as a source of anions which are non- or only weakly co-ordinating with the Group VIII metal under the conditions of the copolymerization. Typical additional components are, for example, protic acids, Lewis acids, acids obtainable by combining a Lewis acid and a protic acid, and an aluminoxane.

The amount of the additional component which functions during the copolymerization as a source of anions which are non- or only weakly co-ordinating with the Group VIII metal, when present, is preferably selected in the range of 0.1 to 50 equivalents per gram atom of Group VIII metal, in particular in the range of from 0.5 to 25 equivalents per gram atom of Group VIII metal. However, the aluminoxanes may be used in such quantity that the molar ratio of aluminium to the Group VIII metal is in the range of from 4000:1 to 10:1, preferably from 2000:1 to 100:1.

The amount of such a catalyst composition used in the said copolymerization of the invention may vary between wide limits. Recommended quantities of catalyst composition are in the range of  $10^{-8}$  to  $10^{-2}$ , calculated as gram atoms of Group VIII metal per mole of olefinically unsaturated compound to be copolymerized



with carbon monoxide. Preferred quantities are in the range of  $10^{-7}$  to  $10^{-3}$  on the same basis.

A said copolymerization process employing a catalyst composition described above may be carried out in the presence of a liquid diluent, but it may also be carried out as a gas phase process. If it is carried out in the presence of a liquid diluent, preferably a liquid diluent is used in which the copolymer to be prepared forms a separate, liquid or solid phase, in which case a diluent may be selected in which the copolymer is insoluble or virtually insoluble. A solution polymerization may be carried out in a liquid diluent in which the copolymer to be prepared is soluble. Examples of liquid diluents are water, ketones (e.g. acetone), chlorinated hydrocarbons (e.g. chloroform or dichloromethane), aromatics (e.g. toluene, benzene, chlorobenzene), and, preferably, protic organic diluents, such as lower alcohols (e.g. methanol and ethanol) and alkanoic acids, for example acetic acid. Mixtures of liquid diluents may be used as well, for example protic diluents may comprise an aprotic diluent. Protic organic diluents may contain water.

Generally, unless otherwise stated in this specification, the term "lower" indicates that the organic compound to which it refers contains at most 6 carbon atoms.

The diluent may comprise water and an alkanol, preferably a  $C_{1-4}$  alkanol, in particular ethanol and, especially, methanol. The ratio of water to alkanol is preferably in the range of 1:0.1-200, more preferably in the range of 1:0.3-10, by volume.

The diluent may comprise water and an alkanoic acid, preferably having from 2 to 5 carbon atoms, preferably acetic acid. The ratio of water to the alkanoic acid is

suitably in the range 1:10-10:1, preferably 1:10-3:1, especially 1:5-2:1, by volume.

The diluent may comprise an alkanol, as defined above, and an alkanoic acid, as defined above. The ratio of the alkanol to the alkanoic acid as added is suitably in the range 1:1 to 20:1, preferably 5:1 to 15:1, by volume.

The diluent may comprise water, an alkanol, as defined above, and an alkanoic acid, as defined above, the relative proportions of these components being within the definitions given in each of the three preceding paragraphs.

The diluent may comprise an ester of an alkanol as defined above and an alkanoic acid, as defined above.

An especially preferred diluent comprises an alkanol, as defined above, an alkanoic acid, as defined above, and an ester of an alkanol and an alkanoic acid (preferably of the same alkanol and alkanoic acid), in water. A preferred mixture has the following relative proportions, by volume: alkanol 3-20; water 1-15; alkanoic acid 1; ester 1-10. An especially preferred mixture has the following relative proportions by volume: alkanol 5-12; water 4-10; alkanoic acid 1; ester 2-6. Especially preferred is 8-9; 5-6; 1; 3-4, as such mixtures represent under the prevailing conditions equilibrium mixtures of the ester forming/ester hydrolysis equilibrium.

Suitably the ligand is in salt form, for example in the form of a metal salt, such as an alkali or earth alkaline metal salt.

A salt (additional to the ligand when the ligand is in salt form) for example an alkali metal salt, notably sodium sulphate (which may be a by-product of a prior sulphonation reaction) or sodium acetate, may advantageously be present. A salt may be present in an

amount of 1-80, preferably 2-30, mol per mol ligand.  
Salts of protic acids may be useful.

Alternatively or additionally a base may advantageously be present (additional to any base needed to neutralize a protonated-form ligand). A suitable base is an alkali metal hydroxide. A base may suitably be present in an amount of 1-80, preferably 2-30, mol per mol ligand. A compound which is a salt and which functions as a base may be employed.

When a said copolymerization process is carried out as a gas phase process it is preferred to use a catalyst system supported on a solid carrier, usually in order to facilitate the introduction of the catalyst composition into the reactor.

Suitable carrier materials may be inorganic, such as silica, alumina or charcoal, or organic such as cellulose or dextrose. Furthermore a polymer material may be used as carrier, such as polyethene, polypropene or, in particular, copolymers of carbon monoxide with an ethylenically unsaturated compound, for example linear alternating copolymers of carbon monoxide with ethene or carbon monoxide with ethene and propene or butene-1.

Conveniently the carrier is impregnated with a solution of the catalyst system in a suitable liquid. It will be appreciated that the amount of liquid used is relatively small, so that any excess thereof can easily be removed before or during the initial stage of the copolymerization process. On the other hand it has been observed, that the addition of a minor amount of liquid during the copolymerization process has a delaying effect on the deactivation rate of the catalyst, the quantity of liquid being so small that the gas phase is the continuous phase during the polymerization. The quantity of liquid is in particular selected such that it is 20-80% by weight, more in particular 40-60% by weight, of

the quantity which is sufficient to saturate the gas phase under the conditions of the polymerization. Polar liquids are preferred, such as lower alcohols, for example methanol and ethanol, lower ethers such as diethylether, tetrahydrofuran or the dimethylether of diethylene glycol (diglyme) and lower ketones such as acetone and methylethylketone.

The copolymerization may also be carried out as an emulsion or solution polymerization reaction.

The presence of a small amount of hydrogen gas may assist the polymerization reaction.

The performance of such a Group VIII metal catalyst composition in a said copolymerization process may be improved by introducing an organic oxidant, such as a quinone or an aromatic nitro compound. Preferred oxidants are quinones selected from the group consisting of benzoquinone, naphthoquinone and anthraquinone. When the process is carried out as a gas phase process, the quantity of oxidant is advantageously in the range of from 1 to 50, preferably in the range of from 1 to 20 mole per gram atom of metal of Group VIII.

A said copolymerization process is usually carried out at a temperature between 20 and 200 °C, preferably at a temperature in the range of from 30 to 150 °C, and usually applying a pressure between 0.2 and 20 MPa, pressures in the range of from 1 to 10 MPa being preferred.

The copolymer may be recovered from a said copolymerization mixture by any suitable conventional technique. For example solvent(s) may be evaporated off, and condensed and recycled if wished. If suitable, the polymer may be recovered by filtration or centrifugation. An advantageous method which may sometimes be used with the preferred solvents of this invention (comprising water and/or an alkanol and/or an alkanolic acid and/or an

ester) is to cool the reaction mixture, adding water if necessary to cause it to separate into two phases. This typically occurs around or above ambient temperature, for example at 10-50 °C, preferably 20-40 °C. The diluent rich layer has been found to contain the major amount of catalyst and may simply be re-used, with some recharging with additional catalyst, if desired. A lesser amount of catalyst can sometimes be extracted from the polymer rich layer, and re-used. The polymer is recovered from the polymer rich layer.

It has been found that a copolymerization process in accordance with the present invention offers surprisingly good rates of reaction. The process exhibits a further advantage in that catalyst recycling is facilitated, as mentioned above. Further, a polymerization product having a better polymer morphology (bulk density) can be obtained, if the process is carried out as a suspension copolymerization process.

Olefinically unsaturated compounds which can be used as monomers in the copolymerization process of the invention include compounds consisting exclusively of carbon and hydrogen and compounds which in addition comprise hetero atoms, such as unsaturated esters. Unsaturated hydrocarbons are preferred. Examples of suitable monomers are lower olefins, i.e. olefins containing from 2 to 6 carbon atoms, such as ethene, propene and butene-1, cyclic olefins such as cyclopentene, aromatic compounds such as styrene and alpha-methylstyrene and vinyl esters, such as vinyl acetate and vinyl propionate. Of course, a mixture of olefins may be used.

Generally, the molar ratio of on the one hand carbon monoxide and on the other hand the olefinically unsaturated compound(s) used as monomer is in the range of 1:50 to 50:1, preferably 1:5 to 5:1. More preferably

the molar ratio is in the range of 1:2 to 2:1, substantially equimolar ratios being preferred most.

Copolymers are preferably prepared in which the units originating from carbon monoxide on the one hand and the units originating from the olefinically unsaturated compound(s) on the other hand occur in an alternating or substantially alternating arrangement. The term "substantially alternating" will be understood by the skilled person to mean the molar ratio of the units originating from the carbon monoxide to the units originating from the olefinically unsaturated compound(s) is above 35:65 in particular above 40:60. When the copolymers are alternating this ratio is 50:50.

Linear copolymers of carbon monoxide and one or more olefinically unsaturated compound(s) which are alternating or substantially alternating, can be produced in a wide range of molecular weights.

For high molecular weight copolymers prepared by the process of the invention, the limiting viscosity number (LVN), or intrinsic viscosity, of the copolymers is indicative of the molecular weight thereof. A high LVN indicates a high molecular weight copolymer and a lower LVN indicates a lower molecular weight copolymer. The LVN is calculated from determined viscosity values, measured for different copolymer concentrations in m-cresol at 60 °C. High molecular weight copolymers have an LVN in the range of from 0.2 to 10 dl/g, in particular, from 0.4 to 8 dl/g, more particularly from 0.6 to 6 dl/g.

A high molecular weight copolymer is usually a solid at the temperatures generally used for producing the copolymer, for example ambient temperature. High molecular weight copolymers generally have a melting point above 150 °C, as determined by differential scanning calorimetry (DSC). They are particularly suitable as a thermoplastic for fibres, films or sheets,



or for injection moulding, compression moulding and blow moulding applications. Such a high molecular weight copolymer may be used for applications in the car industry, for the manufacture of packaging materials for food and drinks and for various uses in the domestic sphere.

A lower molecular weight copolymer includes a polymer having a number average molecular weight within the range 200-20,000, preferably in the range 500-10,000, more preferably in the range 1000-5000, as determined by gel permeation chromatography, using polystyrene standards.

A lower molecular weight copolymer can be liquid, or flowable under low pressure or shear, or solid at the temperatures generally used for processing the copolymer for example ambient temperature. Such copolymers having a high ethylene content may tend to be solid.

For copolymers of lower molecular weight the copolymerization process can generally employ ethene in admixture with propene or an alpha-C<sub>4-6</sub> olefin, preferably straight chain. Examples of suitable olefins are 1-hexene, 1-pentene, 1-butene and, especially 1-propene. Suitably the C<sub>3-6</sub> olefin is present in an amount at least 20 mol%, preferably at least 30 mol%, of the total olefin content of the polymer. The balance is suitably ethene.

In the case of high molecular weight copolymers a higher proportion of ethene is preferred. For such copolymers ethene is suitably the only olefinically unsaturated component or the major one. In high molecular weight linear, alternating copolymers of carbon monoxide, ethene and a C<sub>3-6</sub> olefin, the molar ratio of the C<sub>3-6</sub> olefin to ethene content in the copolymer is typically above 1:100, preferably in the range from 1:100 to 1:3, more preferably in the range of from 1:50 to 1:5.

International patent application No. WO 96/13549 discloses a suitable method of preparation of lower molecular weight copolymers comprising monomers of carbon monoxide and an olefinically unsaturated compound, and examples of use of the resultant copolymers, and is incorporated herein by reference. The presence of carbonyl groups in the polymer may facilitate many cross-linking reactions, and the lower molecular weight copolymers may be useful in curable resin compositions.

There are several methods of preparing an appropriate sulphonated ligand for use in a copolymerization reaction as described above.

A conventional method of sulphonating molecules involves treatment with fuming sulphuric acid, or oleum. However, this method of sulphonation is problematic in that, apart from the general undesirability of working with oleum, it is difficult to control the selectivity of the sulphonation process and mixtures of products, including undesired phosphine oxidation products, may be obtained.

A further known method of sulphonation involves mixing the compound to be sulphonated with a mixture of orthoboric acid and concentrated sulphuric acid, followed by dropwise addition of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  at a temperature of around  $0^\circ\text{C}$ . This method is set out in several patent specifications including European patent applications numbers 632 047, 704 450 and 704 451. An advantage claimed for this method is that the sulphonation is more selective and that undesired phosphine oxidation products are minimal.

Preferably, however, the ligands used are made by a new sulphonation method, which employs mild sulphonation conditions and does not require orthoboric acid. In a further aspect, the present invention relates to a process for sulphonation as defined in claim 15,

hereinafter. The new sulphonation method is suitably carried out in the substantial absence of orthoboric acid, and using, as sulphonating agent, sulphuric acid of concentration at least 85 %wt or oleum of grade  $\leq$  15 %wt.

5 Reference to oleum of grade  $\leq$  15% denotes that up to 15% of the total weight of the  $\text{SO}_3/\text{H}_2\text{SO}_4$  composition is provided by the  $\text{SO}_3$  component; sulphuric acid of concentration at least 85% denotes that at least 85% of the total weight of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  is provided by the  $\text{H}_2\text{SO}_4$   
10 component. Preferably, the sulphonating agent comprises sulphuric acid of concentration at least 90%, more preferably at least 92%, most preferably at least 94%, and especially at least 95%. When the sulphonating agent comprises oleum this is preferably oleum of grade  $\leq$  10%,  
15 most preferably oleum of grade  $\leq$  5%. Preferably, however, sulphuric acid of concentration at most 98%, as opposed to oleum, is used as the sulphonating agent.

The new sulphonation method is preferably carried out in the substantial absence of a boron-containing acid.  
20 The phrases "in the substantial absence of" used in relation to orthoboric acid and a boron-containing acid are herein defined to mean that the sulphonating agent generally comprises less than 5% of the boron-containing acid, preferably less than 2%, most preferably less than  
25 0.5%, in particular less than 0.1% by weight in the reaction mixture. Preferably there is no boron-containing acid in the reaction mixture.

Suitably, the new sulphonation method is carried out at a temperature in the range 0-100 °C, preferably  
30 10-60 °C, especially 20-40 °C. Preferably the method is carried out without external heating.

The new sulphonation method will generally be carried out for sufficient time to achieve effective sulphonation, for the conditions and starting materials

selected. This may be for at least 3-12 hours, depending on the conditions and starting materials selected.

Suitably, the new sulphonation method is carried out for no more than 50 hours, preferably for no more than 24 hours, more preferably for no more than 6 hours.

The new sulphonation method may be carried out in an inert atmosphere, most preferably of nitrogen. In some cases this appears to assist in avoiding undesired products or oxidation at the phosphorus atom(s). In other cases it appears not to make a difference. Simple trial and error will enable the skilled person to determine whether there is advantage in using an inert atmosphere.

Preferably the sulphonating agent is present in considerable excess over the compound to be sulphonated, on a molar basis, in the new sulphonation method. Suitably the ratio of  $\text{H}_2\text{SO}_4$  (calculated on the basis of the sulphur content of sulphuric acid or of oleum) to the compound to be sulphonated is at least 5:1, preferably at least 10:1, most preferably at least 35:1, on a mol:mol basis. For practical reasons this ratio is typically at most 10,000:1, more typically at most 1000:1, on the same basis.

Suitably the new sulphonation method does not employ an additional solvent; that is, the sulphuric acid or oleum serves as sulphonating agent and as solvent.

Using the new sulphonation method mild sulphonation conditions can be employed to obtain target sulphonated compounds in good yields within reasonable timescales, and with low production of undesired side products, such as phosphine oxides.

A sulphonated compound or a salt thereof, whether made by the new method or a known method, may be separated from a sulphonation mixture by conventional methods, for example employing an alkali metal hydroxide, as described above. However, the compound is preferably

separated by a new work-up method which comprises, at the end of the sulphonation method, whether a known sulphonation method or the new sulphonation method, isolating the sulphonated product as a sulphonic acid from the reaction mixture, the isolating step comprising contacting the reaction mixture with a precipitating agent for the sulphonic acid, and separating the sulphonic acid as a solid from the resulting liquid. In a further aspect the present invention relates to a process for preparing a ligand, which process comprises the steps (a) and (b) as defined in claim 14, hereinafter.

An advantage of the new work-up method is that it does not need neutralisation of any acid present in the sulphonation reaction mixture and that it comprises less steps than the prior art methods.

The precipitating agent is preferably water, but organic compounds which comprise a hetero atom such as oxygen, nitrogen or sulphur and which have typically up to 6 carbon atoms are also suitable, as well as mixtures thereof and mixtures with water.

In the new work-up method, preferably the reaction mixture is cooled. In principle the reaction mixture can be lowered to any temperature at which it does not freeze.

In some embodiments of the new work-up method contact with water alone even without lowering of the temperature causes rapid precipitation of the sulphonic acid which can be removed by filtration, and washed if desired. In such embodiments the reaction mixture may be poured into water at room temperature, then filtered. In other embodiments when the temperature is to be lowered it may be advantageous to pour the reaction mixture into water at room temperature, then to cool the resultant mixture. In yet other, more preferred, embodiments in which the temperature is to be lowered, the reaction mixture may be



poured into chilled water, or more preferably, into ice or ice/water, to effect the contacting with water and the cooling together.

5 In some embodiments of the new work-up method the contact with water and lowering of the temperature, if carried out, causes slow precipitation of the sulphonated compound, which can be removed by filtration, and washed if desired. In some embodiments the contact with water alone may cause immediate precipitation, but subsequent  
10 cooling may assist in causing further precipitation. In all such embodiments in which precipitation is not rapidly completed there is preferably a period for which the reaction mixture is held at the lowered temperature, subsequent to the contacting with water. This may be an  
15 extended period, suitably at least 8 hours, preferably at least 16 hours.

In the new work-up method, when the temperature of the reaction mixture is lowered, it is preferably lowered to 10 °C or less; preferably to 5 °C or less. Whilst the  
20 temperature could be lower, for example down to -10 °C, or -25 °C, or even less, it is convenient to use ice or ice/water, and so the lowered temperature is preferably about 0 °C.

Generally, in the new work-up method, the amount of  
25 water with which the sulphonation reaction mixture is mixed can affect the rate and/or degree of crystallisation of the sulphonated product. This can be determined by trial and error. However a ratio of the reaction mixture to water within the range 1:1 to 1:15, preferably 1:2 to 1:10, by volume, is generally suitable.  
30 The term "water" used in the definitions of this specification may be taken to include ice.

The water used to contact the reaction mixture in the new work-up method is preferably reasonably pure.  
35 Demineralised water is suitable.



The statements of the preceeding five paragraphs which relate to the use of water or ice are in an analogous way applicable to embodiments in which another precipitating agent or mixture is used instead of water.

5       The effectiveness of the new work-up method is surprising. It was not expected that the sulphonated compounds would be less soluble in water/sulphuric acid mixtures, than in sulphuric acid alone. Indeed, they appear to be less soluble in water/sulphuric acid  
10       mixtures, than they are in water alone, and in sulphuric acid alone.

      The new work-up method is, clearly, simple and convenient. Furthermore experiments have shown it to be an advantageous method in terms of product yield and/or  
15       purity. The product of the new work-up method is in acidic form. When water is involved the product has one or more groups of the general formula  
-SO<sub>3</sub>H(H<sub>2</sub>SO<sub>4</sub>)<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub>. x may typically be in the range 0-1, especially 0-0.5. y may typically be in the range 0-7,  
20       especially 0.5-6. Further, the yield achieved using the new work-up method has been similar to or exceeded that achieved by the prior art multi-step work-up method, e.g. employing sodium hydroxide, assuming like-for-like sulphonation methods.

25       The new sulphonation method and/or the new work-up method can be used to produce and/or isolate compounds of general formula I having phosphorus atoms M<sup>1</sup> and M<sup>2</sup>, and wherein in an aryl group which has a substituent of general formula -S(O)<sub>n</sub>-X, n represents 2 and R<sup>1</sup> has at  
30       least one further substituent independently selected from hydroxy, alkoxyalkoxy and, especially, alkoxy. The definitions of preferred ligands given above apply, within this definition.

Preferably the catalyst compositions used in the methods of this invention employ as ligands sulphonated compounds made by the new sulphonation method, and isolated by the new work-up method.

5 The invention is illustrated by the following examples. In these examples sulphuric acid (95-97 wt%), 30% sulphur trioxide solution in sulphuric acid (i.e. "30% oleum") and solid 98% purity boric acid ( $H_3BO_3$ ) were purchased in p.a. grade from Merck or Aldrich and p.a. grade solvents were used. The sulphonation reactions were carried out without application of external heat (although in practice at the addition rates employed the temperature of some reaction mixtures may rise to 40-50 °C because of exotherms). The water or ice used in 10 the work-up was demineralised. Product confirmation of ligands described below was by  $^1H$ -,  $^{31}P$ -,  $^{13}C$ -NMR and elemental analysis. The position of the sulphonyl groups was determined by the technique PFG-HMQC (Pulse Field Gradient Heteronuclear Multiple Quantum Coherence).

#### 20 EXAMPLE 1

##### Preparation of 1,3-bis[bis(2-methoxy-5-sodiumsulphonato phenyl)phosphino]propane (BDOMPP-S)

Orthoboric acid ( $H_3BO_3$ , 3.2 g, 51.7 mmol) was added to sulphuric acid (30 ml) and the mixture was stirred until a homogeneous solution was obtained. Subsequently, 1,3-bis[bis(2-methoxyphenyl)phosphino]propane (BDOMPP, 7.3 g, 13.7 mmol) was added. The reaction mixture was cooled to 0 °C and a solution of 30% oleum (150 ml) was added dropwise, whilst the temperature of the reaction mixture was maintained between 0 and 5 °C. After addition was complete, stirring was continued at ambient 30 temperature for 48 hours. The mixture was then hydrolysed by addition of ice (400 g). The acidic reaction mixture was then neutralised by addition of a 25 wt% solution of

sodium hydroxide in water. The neutralised mixture was concentrated by evaporation of water at 75 °C and 200 mbar (20 kPa) pressure until a white suspension was formed. Methanol (750 ml) was then added to the mixture, which was then stirred for 15 minutes. The residual precipitate, consisting mainly of sodium sulphate, was removed by filtration. After removal of the solvent methanol, by evaporation under a vacuum, the residual white solid still contained a significant amount of sodium sulphate. Therefore, a second extraction with methanol was carried out by first dissolving the impure white solid in methanol followed by removal of non-dissolved salt by filtration and subsequent removal of methanol by evaporation under vacuum.

Elemental analysis of the end product as isolated gave the following results: carbon 12.89 %w; hydrogen 2.81 %w; phosphorus 2.81 %w; sulphur 15.42 %w; sodium 17.92 %w. The elemental analysis corresponds to a molecular structure: 1BDOMPP-S, 29.7 H<sub>2</sub>O, 7.6 Na<sub>2</sub>SO<sub>4</sub>. It was calculated that a 33.7 wt% yield of BDOMPP-S as a sodium salt was obtained.

#### EXAMPLE 2

##### Preparation of a BDOMPP-S based catalyst

Palladium acetate (5.0 mg) and BDOMPP-S (obtained in accordance with Example 1 above, 65.9 mg) were dissolved in acetone (5 ml), then water (5 ml) was added. After 1 hour, neat trifluoroacetic acid (10.1 mg) was added.

A clear yellow solution was obtained, which was used to catalyse the copolymerization reaction described in Example 3 below.

#### EXAMPLE 3

##### Polymerization reaction using BDOMPP-S based catalyst

The polymerization reaction was carried out in a 350 ml magnetically stirred steel batch autoclave. The

reactor was charged with 129 ml of a MeOH/H<sub>2</sub>O/HOAc/MeOAc mixture (45.4:29.5:5.3:19.6, v/v). After purging the reactor with nitrogen, 60 g of propylene was added thereto. The reactor was thereafter pressurised with 7 bar (0.7 MPa) of hydrogen gas and 1 bar (0.1 MPa) of carbon monoxide. The mixture was subsequently heated to 89 °C and 30 bar (3.0 MPa) of a 80/20 v/v CO/ethene mixture gas was added to the autoclave.

After stabilization of temperature and pressure, all of the BDOMPP-S based catalyst produced in accordance with Example 2 above, was injected into the reactor to start the reaction. The catalyst system was flushed with 10 ml of acetone to ensure quantitative catalyst injection. The reactor temperature increased to 91 °C. The pressure was kept constant by continuous addition of an 80/20 v/v CO/ethene mixture gas.

After 3 hours the reaction was stopped. The flow of mixture gas was then stopped by blocking the gas supply then the reactor was cooled rapidly down to room temperature and then the gases that did not react were vented until atmospheric pressure was obtained. The reactor content was subsequently transferred to a rotavapor, where the solvents were removed under reduced pressure (60 mbar (6.0 kPa) to 1 mbar (0.1 kPa)) at 70 °C and the isolated polymer was weighed and analyzed for molecular weight and ethene content.

Reaction rate data was calculated on the basis of gas flow uptake and on the basis of average product weight. The results are summarised in Table 1 below.

#### EXAMPLE 4 (comparative)

##### Polymerization reaction using a BDOMPP based catalyst

A catalyst was prepared by dissolving 5.0 mg of palladium acetate and 12.5 mg of BDOMPP in 10 ml of acetone. After 1 hour, 10.1 mg of trifluoroacetic acid was added. The resulting clear yellow liquid was used to

start the following oligomerisation reaction within 30 minutes of addition of the trifluoroacetic acid.

The catalyst was then used in place of the BDOMPP-S based catalyst of Example 2 in a repeat of the polymerization reaction of Example 3. Again, the reaction rate data was calculated and is set out in Table 1.

The data set out in Table 1 clearly illustrates that the reaction rate and the product yield is more than twice as high as a result of use of a catalyst comprising a sulphonated ligand than the reaction rate or product yield when the reaction rate is carried out with a catalyst comprising a corresponding, but non-sulphonated, ligand.

Table 1

Property	BDOMPP (Ex. 4)	BDOMPP-S (Ex. 3)
Initial rate <sup>a</sup> (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	6.1	14.3
End of run rate <sup>a</sup> (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	4.2	11.5
Yield (g)	29.7	70.0
Average rate <sup>b</sup> (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	4.2	9.9
Mn (Dalton)	2869	3284
Mol% ethene <sup>c</sup>	37	33

a - initial rate and end of run rate calculated on bases of gas flow and on Pd intake.

b - average rate calculated on base of polymer yield on Pd intake.

c - mol% based on total olefin content of the polymer.

EXAMPLE 5Recycling the catalyst

The reactor of a 350 ml, magnetically stirred AISI 316 steel batch autoclave was charged with 129 ml of a MeOH/H<sub>2</sub>O/HOAc/MeOAc mixture (45.5:29.5:5.3:19.6 v/v). After purging the reactor with nitrogen, 60 g of propylene was added. The reactor was thereafter pressurised with hydrogen gas at 7 bar (0.7 MPa) and carbon monoxide at 1 bar (0.1 MPa) pressure. The mixture was heated to 89 °C and 30 bar of a 80/20 v/v mixture of carbon monoxide and ethene was added to the reactor. Total reactor pressure was 65-67 bar (6.5-6.7 MPa). After stabilisation of temperature and pressure, the catalyst, as prepared in accordance with Examples 1 and 2 above, was injected to start the oligomerisation reaction. The reactor was flushed with 10 ml of acetone to ensure quantitative catalyst injection. The reactor temperature increased to 91 °C. The pressure was kept constant by continuous addition of a 80/20 v/v mixture of carbon monoxide and ethene gas.

After three hours the reaction was stopped by steps taken in the following order: first the flow of the mixture gas was stopped by blocking the gas supply, then the reactor was cooled down to room temperature and the gases that did not react were vented until atmospheric pressure was obtained. The reactor content was subsequently transferred to a separation funnel. After approximately 1 hour the two phases were separated and weighed. The top layer was used to charge the reactor, the bottom layer was washed with the equilibrium solvent mixture MeOH/H<sub>2</sub>O/HOAc/MeOAc (45.5:29.5:5.3:19.6 v/v), with a volume of  $V(\text{wash}) = V(\text{reactor solvent}) - V(\text{top layer})$ .



This mixture of the bottom layer and the wash-solvent were allowed to settle and were separated after approximately 1 hour. A second top layer and bottom layer were formed. Both layers were weighed. The reactor, already containing the first top layer, was charged with the second top layer. If needed, the volume was brought to the initial solvent volume of 129 ml. The new bottom layer containing polyketone product was transferred to a rotavapor. The solvents were removed at a reduced pressure of 1 mbar (0.1 kPa) at 70 °C and the isolated polymer was analysed for molecular weight and ethene content.

The solvent mixture in the reactor was used to perform the same experiment again. However, this time no catalyst was injected. Two recycles were carried out by this method. The results of this experiment are labelled Experiment A in Table 2 below.

A variant of this procedure involves injecting extra catalyst into the system compensating for the loss of active catalyst during the recycle experiments. Again two recycles were performed by this method, 34 %wt of fresh catalyst being added at the start of each such recycle. The results are labelled Experiment B in Table 2 below.

Table 2

Property	Experiment A			Experiment B		
	Initial	1st recycle	2nd recycle	Initial	1st recycle	2nd recycle
Initial rate <sup>a</sup> (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	10.4	6.9	4.8	11.0	9.9	9.0
End of run rate <sup>a</sup> (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	8.5	5.3	3.4	8.8	7.1	6.4
Average rate <sup>b</sup> (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	7.5	6.7	4.8	7.9	8.0	8.2
Yield (g)	56.4	50.3	35.8	58.0	58.9	59.9

a - initial rate and end of run rate calculated on bases of gas flow and on Pd intake of initial cycle

b - average rate calculated on bases of polymer yield of bottom layer and on Pd intake of initial cycle

Table 2 shows that without addition of extra fresh catalyst the product yield declines from 56.4 g of polymer to 35.8 g of polymer in the second recycle. This is likely to be caused by a combination of catalyst deactivation and the loss of active species with the polyketone polymer via the bottom phase.

Comparison of initial and end of run reaction data gives an indication of the catalytic decay during each cycle. It also illustrates the decline in activity between a specific cycle and the preceding cycle. Based on the difference in these activity values between the cycles it was concluded that approximately 66% of the activity is maintained by recycling the catalyst species. It was therefore concluded that addition of 34% of fresh catalyst should counteract that decline.

Table 2 illustrates that by addition of 34% of fresh catalyst, product yield in the first, second and third cycle were of a similar order of magnitude. This illustrates that addition of 34% catalyst between the first and second cycles and the second and third cycles was sufficient to counteract the decline in activity of the recycled catalyst.

#### EXAMPLE 6

##### Investigation of effects of added base or salt

Firstly a protonated ligand was prepared as follows:

BDMPP (22.5 g) was added to sulphuric acid (110 ml). The mixture was stirred for 24 hours at ambient temperature under a nitrogen atmosphere. The reaction mixture was then poured into water (1000 ml, room temperature) and cooled. After storage at 4 °C overnight a white precipitate was present. The precipitate was filtered and washed twice with methyl ethyl ketone (2 x 250 ml). After drying BDMPP-S in protonated form, 4.1 H<sub>2</sub>O (32.7 g, 83%) was obtained.

- A number of experiments were carried out under different reaction conditions, and employing as diluent methanol/water/acetic acid/methyl acetate equilibrium mixtures, following the procedure set out in Example 3.
- 5 The experiments are summarised, and the results given, in Table 3 below. Experiments were included using ligands of which the sulpho groups were neutralised in situ with sodium hydroxide, or in the presence of sodium sulphate (a constituent of the earlier salt-form examples).

Table 3

Experiments with BDOMPP-S (protonated form), and varying amounts of sodium hydroxide and/or with sodium sulphate.

Catalyst	BDOMPP-S	BDOMPP-S + 4.02 mol NaOH per mol ligand	BDOMPP-S + 6.12 mol NaOH per mol ligand	BDOMPP-S + 8 mol NaOH per mol ligand	BDOMPP-S + 6.12 mol NaOH per mol ligand + 53 mg Na <sub>2</sub> SO <sub>4</sub>
solvent	MeOH 61 ml Water 34 ml HOAc 7 ml MeAc 27ml	MeOH 61 ml Water 34 ml HOAc 7 ml MeAc 27 ml	MeOH 61 ml Water 34 ml HOAc 7 ml MeAc 27 ml	MeOH 61 ml Water 34 ml HOAc 7 ml MeAc 27 ml	MeOH 61 ml Water 34 ml HOAc 7 ml MeAc 27 ml
propene C <sub>3</sub> = (g)	61.2	60.9	60.1	62.2	62.4
pH <sub>2</sub> (bar)	4	4	4	4	4
pCO (bar)	1	1	1	1	1
pCO/C <sub>2</sub> = (bar) 80/20 %v	25	25	25	25	25
p total (bar)	69	68	69	69	69
T (°C)	100	100	100	100	100
time (h)	3	3	3	3	3

Table 3 (cont'd)  
Experiments with BDOMPP-S (protonated form), and varying amounts of sodium hydroxide and/or with sodium sulphate.

Catalyst	BDOMPP-S	BDOMPP-S + 4.02 mol NaOH per mol ligand	BDOMPP-S + 6.12 mol NaOH per mol ligand	BDOMPP-S + 8 mol NaOH per mol ligand	BDOMPP-S + 6.12 mol NaOH per mol ligand + 53 mg Na <sub>2</sub> SO <sub>4</sub>
yield (g)	47	54	63	71	79
av. rate (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	6.7	7.7	8.9	10.1	11.2
Mn	2914	2457	2299	2264	2228
mol % C <sub>2</sub> = on total olefin content of polymer	37.9	35.7	30.5	30.5	30.0



EXAMPLE 7Investigation of solvent effects

Further experiments were performed using the catalyst described in Example 6, following the procedure set out in Example 3. Three experiments were carried out in an equilibrium solvent mixture of methanol, water, acetic acid and methyl acetate and two experiments, under closely similar reaction conditions, were carried out with acetic acid/water solvent mixtures. All experiments were carried out using process conditions directed to preparing a polymer with a target Mn of 3500 and ethylene content of 50% mol, based on the total of olefin incorporated into the polymer product. The experiments are summarized, and results are shown in Table 4 below.

Table 4  
Experiments with BDOMPP-S (protonated form)

Catalyst	BDOMPP-S + 8 mol NaOH per mol ligand	BDOMPP-S + 30 mol Na <sub>2</sub> SO <sub>4</sub> per mol ligand	BDOMPP-S + 30 mol NaAc per mol ligand	BDOMPP-S + 30 mol NaAc per mol ligand	BDOMPP-S + 30 mol NaAc per mol ligand, after 1 hr another 30 mol NaAc per mol ligand
solvent	MeOH 48 g Water 34 g HOAc 7 g MeAc 25 g	MeOH 48 g Water 35 g HOAc 7 g MeAc 25 g	MeOH 48 g Water 34 g HOAc 7 g MeAc 25 g	HOAc 65 g Water 68 g	HOAc 96 g Water 39 g
propene C <sub>3</sub> = (g)	61.1	61.2	61.8	65.0	60.1
pH <sub>2</sub> (bar)	4	4	4	4	4
pCO (bar)	1	1	1	1	1
pCO/C <sub>2</sub> = (bar) 70/30 %v	25	25	25	25	25
p total (bar)	69	69	69	75	70
T (°C)	100	98	97	98	95
time (h)	3	3	3	3	3

Table 4 (cont'd)  
Experiments with BDOMPP-S (protonated form)

Catalyst	BDOMPP-S + 8 mol NaOH per mol ligand	BDOMPP-S + 30 mol Na <sub>2</sub> SO <sub>4</sub> per mol ligand	BDOMPP-S + 30 mol NaAc per mol ligand	BDOMPP-S + 30 mol NaAc per mol ligand	BDOMPP-S + 30 mol NaAc per mol ligand, after 1 hr another 30 mol NaAc per mol ligand
Yield (g)	79	80	85	63	70
av. rate (kg.gPd <sup>-1</sup> .h <sup>-1</sup> )	14.0	14.2	15.1	11.1	12.4
M <sub>n</sub>	3125	3302	3253	4471	4351
mol% C <sub>2</sub> = on total olefin content of polymer	50.3	50.6	49.0	52.1	48.1

EXAMPLE 8Synthesis of BDOMPP-S[Na]<sub>4</sub>Pd(OAc)<sub>2</sub> catalyst

5.20 g of BDOMPP (9.8 mmol) was added to 21 ml of sulphuric acid and stirred for 22 hours at room temperature under a nitrogen atmosphere. The reaction mixture was poured in 100 ml of water and after storage at -20 °C, a white precipitate was formed. After filtration, the resulting solid was washed with 2 portions of acetone (10 ml). After drying, 8.85 g of BDOMPP-S, 3.4 H<sub>2</sub>O, 0.7 H<sub>2</sub>SO<sub>4</sub> was obtained.

The portion was mixed with another portion of BDOMPP-S (0.9% H<sub>2</sub>SO<sub>4</sub>) and after washing with 2 portions of methyl ethyl ketone a white solid was obtained with the composition, BDOMPP-S, 4.1 H<sub>2</sub>O, 0.25 H<sub>2</sub>SO<sub>4</sub>.

A portion of the thus-obtained BDOMPP-S (1.01 g, 1.01 mmol) was dissolved in water (30 ml). Sodium hydroxide (1.62 g, 4.05 mmol) was added. The mixture was stirred for 15 minutes and then added to Pd(OAc)<sub>2</sub> (216 mg, 0.96 mmol) dissolved in acetone (30 ml). The solution, which turned yellow, was stirred at ambient temperature for 2 hours. The solvents were removed under vacuum and the residue was washed with diethyl ether (40 ml) and then acetone (10 ml) to obtain the title compound (860 mg).

EXAMPLE 9Copolymerization of carbon monoxide and ethene using the BDOMPP-S [Na]<sub>4</sub>Pd(OAc)<sub>2</sub>/trifluoroacetic acid catalyst

A suspension of methanol:water (1:1, by volume, 1 litre in total) and a polymer seed powder, which was an alternating carbon monoxide/ethene/propene copolymer (60 g), was placed in an autoclave. The autoclave was heated to 90 °C and pressurized with 25 bar (2.5 MPa) of ethene followed by an additional 25 bar (2.5 MPa) of carbon monoxide. The pressure was maintained constant at

50 bar (5.0 MPa) using a 1:1 mixture of carbon monoxide/ethene.

5 A mixture of BDOMPP-S[Na]<sub>4</sub>Pd(OAc)<sub>2</sub>, as prepared in accordance with Example 8 above, (16.5 mg, 14.2 μmol, 1.5 mg Pd) and trifluoroacetic acid (6.7 μl, 86 μmol) in water (10 ml) was injected into the autoclave. The copolymerization reaction was conducted for 1 hour at 90 °C at a constant pressure of 50 bar (5.0 MPa) carbon monoxide/ethene. The reaction mixture was removed from  
10 the autoclave, filtered and the polymer was dried at 100 mbar (10.0 kPa) pressure and 80 °C. 47.0 g of copolymer was obtained and the average copolymerization rate was 31.3 kg.gPd<sup>-1</sup>.h<sup>-1</sup>.

15 This copolymerization was repeated varying the composition of the solvent. The further results are set out in Table 6 below. Recycling mentioned in Table 5 involved removal of the polymer product by filtration and repeating the copolymerization process using the same catalyst/solvent, without recharge of the catalyst.

Table 5

Copolymerization results with BDOMPP-S[Na]<sub>4</sub>Pd(OAc)<sub>2</sub>/TFA catalyst

Solvent	Yield (g)	Reaction time (h)	Rate (kg.g Pd <sup>-1</sup> h <sup>-1</sup> )	ppm palladium*	seed (%) *
3:1 H <sub>2</sub> O:MeOH	41.4	1.00	27.6	1.50	6
3:1 H <sub>2</sub> O:MeOH recycle	32.2	1.50	14.3	1.50	2
1:1 H <sub>2</sub> O:MeOH	72.5	1.75	27.6	1.50	6
1:3 H <sub>2</sub> O:MeOH	46.7	1.00	31.1	1.50	6

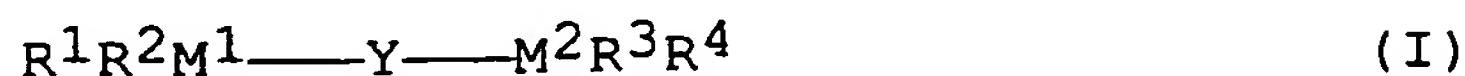
Ratios are vol:vol

\* Relative to the weight of the diluent.



C L A I M S

1. A copolymerization process comprising the step of copolymerizing carbon monoxide and an olefinically unsaturated compound in the presence of a catalyst composition based on a Group VIII metal and a dentate ligand having the general formula



where  $M^1$  and  $M^2$  independently represent one of phosphorous, nitrogen, arsenic and antimony,  $R^1$  represents an aryl group having a substituent of the general formula  $-S(O)_n-X$ , in which  $n$  represents 0, 1 or 2 and  $X$  represents a hydroxy group, which aryl group is optionally further substituted;  $R^2$ ,  $R^3$  and  $R^4$  independently represent an optionally substituted alkyl group or optionally substituted aryl group, on the understanding that at least one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  represents an aryl group having a substituent or a further substituent selected from hydroxy, alkoxy and alkoxyalkoxy; and  $Y$  represents a bridging group; or an ester or salt derivative of such a ligand.

2. A process in accordance with claim 1, characterised in that each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  represents an aryl group having a substituent of the general formula  $-S(O)_n-X$ .

3. A process in accordance with claim 1 or 2, characterised in that each of  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  is a phenyl group having a substituent at the 2-position and a substituent of general formula  $-S(O)_n-X$  at the 5-position.

4. A process in accordance with any one of the preceding claim, characterised in that n is 2.

5. A process in accordance with any one of the preceding claims, characterised in that X represents a hydroxy group or a salt derivative thereof.

6. A process in accordance with claim 5, wherein the ligand is in alkali metal salt form.

7. A process in accordance with any one of the preceding claims, characterised in that both of M<sup>1</sup> and M<sup>2</sup> represent a phosphorus atom.

8. A process in accordance with any one of the preceding claims, characterised in that Y is an organic bridging group containing from 2-4 bridging atoms.

9. A process in accordance with claim 8, characterised in that all of the bridging atoms are carbon atoms.

10. A process in accordance with any one of the preceding claims, characterised in that the Group VIII metal is palladium.

11. A process in accordance with any one of the preceding claims, characterised in that the olefinically unsaturated compound is ethene or a mixture of ethene, and propene or an alpha-olefin having from 4 to 6 carbon atoms.

12. A process in accordance with any one of the preceding claims, wherein a catalyst composition is recovered at the end of the copolymerization and re-used in a further such process.

13. A process in accordance with claim 12, wherein the reaction mixture is cooled to separate it into two phases, adding water if needed to facilitate the separation, one of the phases being rich in the catalyst composition and the other of the phases being rich in the copolymer, wherein the phase rich in catalyst composition is re-used in a further such process.

14. A process in accordance with claim 1, wherein the ligand is prepared by

(a) sulphonating a compound of general formula



5 to form a sulphonic acid derivative thereof; wherein R<sup>1</sup> represents an aryl group which is substituted by one or more groups independently selected from alkoxy, hydroxy and alkoxyalkoxy groups, which aryl group is optionally further substituted; R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> independently  
10 represent an optionally substituted alkyl, optionally substituted alkoxy or optionally substituted aryl group; Y represents a bridging group; and

(b) at the end of the sulphonation step, isolating the resulting sulphonic acid from the reaction mixture, the  
15 isolating step comprising contacting the reaction mixture with water without neutralisation, and separating the sulphonic acid as a solid from the resulting liquid.

15. A process in accordance with claim 1 or 14, wherein the ligand is prepared by sulphonation of a compound of  
20 general formula



to form a sulphonic acid derivative thereof; wherein R<sup>1</sup> represents an aryl group which is substituted by one or more groups independently selected from alkoxy, hydroxy  
25 and alkoxyalkoxy groups, which aryl group is optionally further substituted; R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> independently represent an optionally substituted alkyl, optionally substituted alkoxy or optionally substituted aryl group; Y represents a bridging group; wherein the sulphonation  
30 method is carried out in the substantial absence of a boron-containing acid and using, as sulphonating agent, sulphuric acid of concentration at least 85% or oleum of grade ≤ 15%.

16. A catalyst composition as defined in claim 1.

17. A dentate ligand as defined in claim 1.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/04216

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G67/02 B01J31/16 C07F9/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G B01J C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 280 380 A (SHELL INT RESEARCH) 31 August 1988 (1988-08-31) column 1, line 21 - line 52; claims ---	1-17
A	WO 93 24553 A (SHELL CANADA ET AL.) 9 December 1993 (1993-12-09) page 5, line 17 - line 35; claims ---	1-17
A	EP 0 743 336 A (SHELL INT RESEARCH) 20 November 1996 (1996-11-20) cited in the application page 4, line 25 - line 53; claims ---	1-17
A	US 5 777 087 A (C. KOHLPAINTNER ET AL) 7 July 1998 (1998-07-07) claims --- -/--	1,14,15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

28 August 2000

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# INTERNATIONAL SEARCH REPORT

Intern Application No  
PCT/EP 00/04216

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Interr. Application No

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